

Application of the Pesticide Transport Assessment Model to a Field Study in a Humic Sandy Soil in Vredepeel, The Netherlands

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Abstract: The Pesticide Transport Assessment model (PESTRAS) is a process-oriented model to simulate the fate and movement of water and pesticides in a cropped field soil. The model was evaluated using field data for bromide, ethoprophos and bentazone, collected from a field experiment in a humic sandy soil near Vredepeel, the Netherlands. Model predictions were generally within the 95% confidence intervals of the observations when site-specific model inputs were used. If generic parameter values were used, the model predictions sometimes deviated strongly from the observed data. This was especially true for pesticide degradation properties. The bromide simulations showed that preferential flow was not an important process for this field soil. A significant fraction of the applied ethoprophos disappeared by surface volatilization. The downward movement of this pesticide was slightly overestimated, due to not considering sorption kinetics. The depth-dependence of pesticide transformation was atypical: an important fraction of the applied bentazone was transformed under micro-aerobic to anaerobic conditions in the subsoil. © 1998 SCI

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Key words: modelling; ethoprophos; bentazone; volatilization; transformation; soil pesticide movement

1 INTRODUCTION

During the 1980s it became clear that the total pesticide use per hectare of arable land was high in the Netherlands compared to other European countries.¹ At the same time, results of extensive groundwater monitoring programmes showed approximately 50 pesticides at observable concentrations in the groundwater of western Europe and the USA.^{2–4} For these reasons, the Dutch government released a declaration with the intent of reducing both the total pesticide use and the

emission of pesticides to groundwater, surface water and the atmosphere. These objectives have been worked out in more detail in the Multi-Year Crop Protection Plan.⁵ Models play an important role in the evaluation of this policy plan.⁶ As a part of this evaluation, the pesticide leaching model PESTRAS,^{7,8} in combination with an information system on pesticide use, was applied to obtain quantitative information on pesticide emissions to the groundwater on a regional scale.^{9,10}

Before PESTRAS can be used for quantitative assessment of expected pesticide leaching to the groundwater, its ability to simulate the movement and distribution of pesticides in soil should be evaluated ('model validation'). A crucial part of such a validation study is the comparison of model results with independent field

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observations. In the case of a regional-scale model, such a study should include an evaluation of both the predicted spatial pattern, and the temporal variation of pesticide leaching. However, regional-scale observations of pesticide leaching are scarce or non-existent, and are usually limited to one point-in-time.⁴ As an alternative, the model is applied to a number of field plots where most model inputs can be obtained from direct measurements, and where the fate of a pesticide is measured as a function of time. For validation of a regional-scale model, the field plots should be selected carefully, so that they cover a broad range of soils, pesticides and hydrological conditions.

The main objective for the present study was to evaluate the ability of PESTRAS to simulate the movement and distribution of bromide and two pesticides in the soil system. To achieve this, the model was applied to a data-set collected from a field experiment in a humic sandy soil near Vredepeel, the Netherlands.¹¹ In this model application on-site measured data were available. As many of these model inputs were not available for regional-scale applications, we evaluate the effect of using generic parameter values instead of on-site measured parameter values.

2 MATERIALS AND METHODS

2.1 Field study

The field study was conducted at the experimental farm 'Vredepeel' in the south-eastern part of the Netherlands (51°32'N; 5°52'E) and is described in detail by Boesten and Van der Pas.¹¹ Annual average precipitation is approximately 750 mm, potential evapotranspiration is 530 mm and average temperature 9.3°C. All experiments were carried out at a plot of size 54 × 80 m, which was part of an agricultural field (60 × 160 m). There were drain lines at 1.2 m depth, but all drains were closed during the experiments. The water table resided at 0.5–1.5 m below the soil surface. Table 1 summarizes some general soil properties.

The experimental plot was sown with winter wheat before pesticide and bromide applications. Bromide (sodium bromide solution) and two pesticides (ethoprophos [*O*-ethyl *S,S*-dipropyl

phosphorodithioate] and bentazone [3-isopropyl-1*H*-2,1,3-benzothiadiazin-4-(3*H*)-one 2,2-dioxide]) were sprayed on 22 November 1990 at rates of 111, 3.4 and 0.8 kg AI ha⁻¹, respectively. The wheat crop was harvested in August 1991. After a short bare period, mustard was sown and it was harvested at the end of November 1991.

Soil profile samples were taken from 16 soil columns (diameter 0.1 m) on 1, 22, 42, 103, 214, 278, 347 and 474 days after pesticide application. Sampling depth was down to 1.2 m. After sampling, the columns were sliced into layers, and pesticide and bromide contents and the volume fraction in the liquid phase were determined. Also the gravimetric soil water content and the dry bulk density were determined. Soil samples from one particular layer were pooled to four samples before pesticide analysis. Bentazone was extracted by shaking moist soil with acetone + water (50 + 50 by volume); the supernatant was extracted with dichloromethane and analysed by HPLC (analytical recovery 86–96%; detection limit 1–3 µg dm⁻³). Ethoprophos was extracted with calcium chloride solution (0.01 M) + hexane (50 + 50 by volume) and analysed by GLC/NPD or GLC/FID (recovery 89%; detection limit 0.2–0.5 µg dm⁻³). Sixteen groundwater tubes were installed with filters at 0.8–1.0 m, 1.2–1.4 m and 1.9–2.1 m depth. On each sampling day groundwater samples were taken from the filters situated below the groundwater level. The water samples were combined to four samples and analysed for ethoprophos and bentazone. At the experimental field, soil and air temperatures, rainfall and groundwater level were continuously recorded. Before pesticide application, 70 samples were taken from the top 0.25 m of the soil; the samples were mixed and were used for laboratory experiments on transformation rate and adsorption of both pesticides. At the same time samples were taken from the 0.5–1.0 m and the 1.2–2.0 m soil layers. The latter layer was water-saturated at the time of sampling. These samples were used for laboratory experiments on transformation rates in the subsoil. Duplicate samples (volume 300 cm³) were taken for the determination of the water retention characteristic for the 0.1–0.18, 0.45–0.53 and 0.70–0.78 m soil layers. The unsaturated hydraulic conductivity function was measured using the evaporation method of Wind.¹²

TABLE 1
Selected Properties of the Vredepeel Soil

Soil layer	pH-KCl	Organic matter (%)	Clay (%)	Silt (%)	Sand (%)	Bulk density (kg m ⁻³)
0–0.32 m ^a	5.3	4.90	3	6	91	1315
0.32–1.0 m	4.7	0.23	2	2	96	1666
1.0–2.0 m	4.6	0.25	3	9	88	1700

^a Depth of layer boundary inferred from colour transition in the field.

2.2 The pesticide transport assessment model

For this study, the mechanistic, process-oriented model PESTRAS (Pesticide Transport Assessment) was used.^{7,8} PESTRAS is a one-dimensional, dynamic, multi-layer model for simulating transient flow, hydrodynamic dispersion, equilibrium sorption, transformation, uptake and volatilization of pesticides by plant roots in the unsaturated zone and the uppermost part of the saturated zone. The model consists of three major submodels: (i) hydrology, (ii) heat transport and (iii) pesticide transport, sorption, transformation and volatilization.

2.2.1 Hydrology

The hydrological submodel¹³ uses a finite-difference method to solve the Richards equation:

$$C(h) \frac{\partial h}{\partial t} = \frac{\partial}{\partial z} \left[K(h) \left(\frac{\partial h}{\partial z} + 1 \right) \right] - S_w(h) \quad (1)$$

where C (m^{-1}) is differential water capacity, t (days) is time, z (m) is vertical position, h (m) is soil water pressure head, K (m day^{-1}) is unsaturated hydraulic conductivity and S_w (day^{-1}) is a sink term accounting for water uptake by roots.

The driving force for the water uptake sink term is the potential transpiration, T^* (m day^{-1}). It is calculated from the reference evapotranspiration (ET^*):

$$T^* = f_c (1 - e^{-0.6 \cdot LAI}) ET^* \quad (2)$$

where f_c (—) is an empirical crop factor, LAI ($\text{m}^2 \text{m}^{-2}$) is the Leaf Area Index and ET^* (m day^{-1}) is the potential evapotranspiration according to Makkink.¹⁴ The potential uptake from a specific soil layer is calculated by distributing the potential transpiration over all soil layers using the root length distribution and simulated water contents. Vertical feedback mechanisms are simulated with preferential uptake from layers with high water saturation fractions.¹⁵ The actual water uptake is calculated by multiplying the potential uptake by a dimensionless reduction function for that particular layer.¹⁶

PESTRAS contains several options for the lower boundary condition. In this particular study, a flux condition was chosen:

$$J_{bot} = a_b e^{b_b |H|} + c_b \quad (3)$$

where J_{bot} (m day^{-1}) is the soil water flux through the bottom of the system, H (m) is the groundwater depth, and a_b (m day^{-1}), b_b (m^{-1}) and c_b (m day^{-1}) are parameters.

2.2.2 Heat transport

The model takes into account conductive and convective transport of heat in the soil:

$$\frac{\partial C_h T}{\partial t} = \frac{\partial}{\partial z} \left(\lambda \frac{\partial T}{\partial z} - J_w \rho_w H_w T \right) \quad (4)$$

where C_h ($\text{J m}^{-3} \text{K}^{-1}$) is the specific heat capacity, T (K) is temperature, λ ($\text{J m}^{-1} \text{day}^{-1} \text{K}^{-1}$) is the effective heat conductivity, J_w (m day^{-1}) is soil water flux, ρ_w (kg m^{-3}) is the density of water and H_w ($\text{J kg}^{-1} \text{K}^{-1}$) is the specific heat capacity of water. The upper boundary condition is the air temperature, and the lower boundary condition is a fixed temperature.

2.2.3 Pesticide transport, transformation and sorption

The pesticide fate model considers a three-phase one-dimensional soil column:

$$\begin{aligned} \frac{\partial}{\partial t} (\rho X + \theta c + \varepsilon Y) = & \frac{\partial}{\partial z} \left(\theta D \frac{\partial c}{\partial z} - \theta v c + D_{e, Fi} \frac{\partial Y}{\partial z} - J_p \right) \\ & - S_s - R_s \end{aligned} \quad (5)$$

where ρ (kg m^{-3}) is the dry bulk density of the soil, X (kg kg^{-1}) is the solid-phase mass content, θ ($\text{m}^3 \text{m}^{-3}$) is the volumetric water content, c (kg m^{-3}) is the mass concentration in the liquid phase, D ($\text{m}^2 \text{day}^{-1}$) is the hydrodynamic dispersion coefficient, v (m day^{-1}) is the flow rate of the pore water, ε ($\text{m}^3 \text{m}^{-3}$) is the volumetric air content, Y (kg m^{-3}) is the concentration in the gas phase, $D_{e, Fi}$ ($\text{m}^2 \text{day}^{-1}$) is the effective Fickian diffusion coefficient of gas in soil, J_p ($\text{kg m}^{-2} \text{day}^{-1}$) is the pressure adjustment flux,¹⁷ S_s ($\text{kg m}^{-3} \text{day}^{-1}$) is the rate of plant uptake of the pesticide and R_s ($\text{kg m}^{-3} \text{day}^{-1}$) is the rate of transformation of the pesticide. The hydrodynamic dispersion coefficient is composed of terms from molecular diffusion and dispersion due to mechanical mixing during advection:

$$D = a_l D_o + L |v| \quad (6)$$

where a_l (—) is the soil matrix factor quantifying reduction of diffusion in a porous medium, D_o ($\text{m}^2 \text{day}^{-1}$) is the molecular diffusion coefficient in water, L (m) is dispersivity and v (m day^{-1}) is the flow rate of the pore water. The effective Fickian diffusion coefficient is calculated according to Bakker and Hidding:¹⁸

$$D_{e, Fi} = a_g (\varepsilon - \varepsilon_0) D_{o, Fi} \quad (7)$$

where $D_{o, Fi}$ ($\text{m}^2 \text{day}^{-1}$) is the effective diffusion coefficient of gas in free air, a_g is an empirical parameter and ε_0 ($\text{m}^3 \text{m}^{-3}$) is the air content at a pressure head corresponding to the air-entry value.

Equilibrium sorption onto the soil solid phase is described by the Freundlich equation:

$$X = K_F c^{1/n} \quad (8)$$

where K_F ($\text{m}^{3/n} \text{kg}^{-1/n}$) is the Freundlich sorption coefficient, and $1/n$ is the Freundlich exponent. The Freundlich coefficient is calculated from the coefficient for distributing the substance over organic matter and water, K_{om} ($\text{m}^3 \text{kg}^{-1}$):¹⁹

$$K_f = f_{om} K_{om} c_e^{1-(1/n)} \quad (9)$$

where f_{om} (kg kg^{-1}) is the mass fraction of organic matter, and c_e (kg m^{-3}) is the concentration at which K_F has been calculated (usually 1 g m^{-3}). The dissolved and gaseous phases are assumed to be in equilibrium in accordance with Henry's law:

$$Y = K_H c \quad (10)$$

where K_H ($\text{m}^3 \text{m}^{-3}$) is the Henry coefficient.

The transformation of a pesticide in the soil, R_s , is described by a first-order rate equation:¹⁹

$$R_s = f_T f_p f_z \frac{\ln(2)}{DT_{50}} c^* \quad (11)$$

where f_T , f_p and f_z (—) are reduction factors accounting for the influence of temperature, soil-water pressure head and depth in soil, DT_{50} (days) is the disappearance half-life under reference conditions (i.e. measured in freshly sampled top-soil at a temperature of 293 K, and at a soil-water pressure head of -1 m), and c^* (kg m^{-3}) is the total content of pesticide in the soil system. The reduction factors are described by:

$$f_T = e^{(\gamma(T - T_{ref}))} \quad (12)$$

and

$$f_p = \min(1, (h_{ref}/h)^B) \quad (13)$$

where B (—) and γ (K^{-1}) are empirical parameters, T (K) is the prevailing soil temperature, T_{ref} (K) is a reference temperature (293 K), h (m) is the soil-water pressure head, h_{ref} (m) is a reference soil-water pressure head (usually -1 m), and \min refers to 'minimum of'. The depth-in-soil function, f_z , accounting for depth distribution of microbial activity, is described through a table.

The uptake rate of a pesticide by plant roots from soil, S_s , is described by:

$$S_s = f_{uc} S_w c \quad (14)$$

where f_{uc} (—) is an empirical transpiration stream concentration factor, S_w (day^{-1}) is the sink term accounting

for water uptake by plant roots and c (kg m^{-3}) is mass concentration of pesticide in the liquid phase.

Before the first rainfall, the pesticide is assumed to reside in a thin surface film. Volatilization of pesticide from this thin surface layer is assumed to occur by vapour diffusion through a stagnant air boundary layer of thickness d (m), above which the chemical concentration is zero.²⁰ The mass balance for the surface film can be simplified to

$$\frac{dC}{dt} = -\frac{J_s}{d} \quad (15)$$

where J_s ($\text{kg m}^{-2} \text{day}^{-1}$) is the volatilization flux, which is calculated by

$$J_s = R_v^{-1} Y_s \quad (16)$$

where R_v (day m^{-1}) is the transport resistance and Y_s (kg m^{-3}) is the concentration in the gas phase. During the first rainfall, the pesticide is assumed to enter the soil, and the boundary condition becomes a known concentration at the soil surface. See Freijer *et al.*⁸ for details.

2.3 Derivation of input data

2.3.1 Physical properties

Soil hydraulic properties are represented in PESTRAS by the Mualem and Van Genuchten functions.²¹ The measured data were fitted to these functions, using a non-linear optimization algorithm.²² Parameter l was not optimized. Instead, the average value derived by Mualem²³ was used. Although the saturated hydraulic conductivity was measured, it was not used. Instead, it was obtained by substituting the hydraulic conductivity at a pressure head of -1 m (which was also measured) into the optimized functions. In this way, the extreme variability due to macropore flow at saturation was avoided. Table 2 gives the parameters for the soil hydraulic properties.

The dispersion length was initially set to 0.05 m , which is the average of values found by van Ommen *et al.*²⁴ The soil bulk density was inferred from the dataset, and is listed in Table 1. The pore volume, ϕ , was calculated by multiplying the saturated soil water content by a factor of 1.2. This factor was included to account for the effect of residual air during soil wetting.²⁵ The density of the soil solid phase, ρ_s (kg m^{-3}), was calculated by:

$$\rho_s = \frac{\rho}{(1 - \phi)} \quad (17)$$

The air content at the air-entry value, ε_o , was calculated from $\phi - \theta_\alpha$, where θ_α is the water content at a pressure

TABLE 2
Parameters^a of the Mualem and Van Genuchten Functions to Describe the Soil Hydraulic Properties

Depth (m)	θ_s ($m^3 m^{-3}$)	θ_r ($m^3 m^{-3}$)	α (m^{-1})	n (—)	K_s ($m day^{-1}$)	l (—)	SSR
0–0.32	0.4495	0.0000	21.08	1.3358	0.50	0.5	3.56×10^{-2}
0.32–0.6	0.4051	0.0000	4.97	1.4500	0.15	0.5	4.62×10^{-2}
>0.60	0.2951	0.0000	2.41	1.9910	0.05	0.5	2.78×10^{-2}

^a θ_s is saturated soil water content, θ_r is residual soil water content, K_s is saturated hydraulic conductivity, α , n and l are parameters, and SSR is sum of squares of residuals.

head equal to the air-entry value ($-1/\alpha$). Parameter a_g (eqn (7)) was derived from Freijer²⁵ and was set to 0.5.

2.3.2 Crop-related properties

The reduction function for water uptake was set to 1 (no reduction) for $h > -5$ m, and decreased linearly to 0 between $h = -5$ m and $h = -80$ m. These values were based on a field study for maize.¹⁹ The Leaf Area Index was calculated from the observed soil coverage according to Belmans *et al.*¹⁶ Its maximum value was $5.42 m^2 m^{-2}$ for mature winter wheat and $4.00 m^2 m^{-2}$ for mature yellow mustard. The crop factor, f_c , was taken from Feddes.²⁶ For full-grown winter wheat a crop factor of 1.2 was used, which declined to 0.6 after maturation of the crop. For yellow mustard, a crop factor of 1 was used. The root depth of the mature crops was set to -0.4 m. Root density was assumed to be constant with depth.

2.3.3 Relationship between groundwater level and drainage

No information about the local hydrological situation was available in the data-set, so parameter values for the relationship between groundwater level and drainage could only be obtained by calibration. We used an automated calibration procedure in which the parameters were optimized by minimizing the sum of squares of residuals between the simulated and measured groundwater levels. PESTRAS was coupled to a program based on the Simplex optimization algorithm.²² Approximately 250 runs were required to find the optimum parameter set. Although the Simplex algorithm is not very sensitive to local minima in the parameter space, we repeated the optimization with different initial parameter settings. The first guess of these parameters was taken from De Visser and De Vries.²⁷ They gave the following parameter values for a sandy soil in Brabant: $a_b = -0.00133 m day^{-1}$, $b_b = -1.0 m^{-1}$ and $c_b = -0.0003 m day^{-1}$.

2.3.4 Bromide properties

Bromide was assumed to be conservative with no interactions with the solid and gas phases, so the half-life

was set to 10^{10} days, and K_{om} and K_H were set to zero. The diffusion coefficient of bromide in water was set to $1.6 \times 10^{-4} m^2 day^{-1}$ based on Weast.²⁸ Bromide was initially assumed not to be taken up by plants, thus the transpiration stream concentration factor (f_{uc}) was set to 0.

2.3.5 Pesticide data

Adsorption isotherms were determined at different temperatures with soil sampled from the topsoil.¹¹ The sorption points available in the data-set were fitted to the Freundlich model. Two different fitting procedures were used, i.e. linear regression of log-transformed data, and non-linear curve fitting. Table 3 summarizes the results of the fitting. Notice that there is a distinct difference between sorption of ethoprophos at $5^\circ C$ and $25^\circ C$, both for $1/n$ and K_{om} . We decided to use the $5^\circ C$ sorption isotherm, as this temperature closely resembles field conditions at the time of pesticide application. Notice that the value of $1/n$ is somewhat more affected by the fitting procedure than K_{om} . Although the choice is arbitrary, we used the results from the non-linear curve fitting.

The rate of transformation in the topsoil was measured in the laboratory at 5 and $15^\circ C$ in the case of bentazone and 5 , 15 and $25^\circ C$ in the case of ethoprophos. Soil, 50-g portions for the 0–25 cm layer and 100-g portions for the 50–100 and 100–200 cm layers, was incubated for periods up to 450 days. Initial concentrations in the top layer soil sample were $5.7 mg kg^{-1}$ for ethoprophos and $1.2 mg kg^{-1}$ for bentazone; for the deeper layers the initial concentrations were $12 \mu g kg^{-1}$ and $120 \mu g kg^{-1}$, respectively. Incubation jars were capped with aluminium foil. Soil from the 100–200 cm layer was incubated under waterlogged (5 mm water layer) conditions. Redox measurements in the field showed a fairly constant value of approximately 200 mV during a 6-month period. The incubation method for the 100–200 cm layer was chosen to approximate field conditions, i.e. to have micro-aerobic to anaerobic conditions. First-order rate-constants, k (day^{-1}), were calculated for each temperature using two fitting procedures, i.e. linear regression of ln-transformed data and non-linear curve fitting. With the rate constants obtained for different

TABLE 3
Freundlich Parameters after Linear Fitting of Log-transformed data and Non-linear Curve Fitting of the Original Data

Parameter	Ethoprophos				Bentazone			
	Log-transformed		Non-linear		Log-transformed		Non-linear	
	5°C	25°C	5°C	25°C	5°C	15°C	5°C	15°C
K_{om} (dm ³ kg ⁻¹) ^a	59	86	63	90	2.8	2.6	2.8	2.5
l/n (—)	0.83	0.90	0.81	0.88	0.90	0.86	0.91	0.90
r^2	0.99	0.99	0.98	0.99	0.99	0.99	0.98	0.99

^a Calculated from K_F using the organic matter content of the topsoil.

temperatures, parameter γ (eqn (12)) had to be calculated according to Boesten and Van der Linden.¹⁹ Finally, the half-life at 20°C was calculated with eqn (12). Transformation in the subsoil was measured at one temperature only (10°C), so the half-life in the subsoil at 20°C was calculated using parameter γ for the topsoil. Results shown in Table 4 indicate that the calculated half-lives were strongly affected by the fitting procedure. This is caused by the large scatter in the data-points, as shown by Boesten and Van der Pas.¹¹ In the case of linear regression on ln-transformed data, lower points are given relatively more weight, whereas the opposite is true for non-linear curve fitting. As the choice is rather arbitrary we performed simulations with results from both fitting procedures. The parameter γ was 0.126–0.170 for bentazone, which is outside the range of 50 experiments reviewed by Boesten.²⁹ Probably, the temperature of 5°C chosen as the lower range of temperatures in the transformation experiment was outside the range for which the Arrhenius equation applies, resulting in an overestimation of γ . For ethoprophos, parameter γ was close to the average value reported by Boesten.²⁹ The depth-dependence of transformation is rather curious. Lowest transformation rates were found in the middle soil layer for both pesticides. Independent incubation studies with 2,4-D [(2,4-dichlorophenoxy) acetic acid] and acetate showed the same general depth-

dependence of transformation (Bogte, J. J., pers. comm., 1997), so an experimental artifact could be excluded.

Parameter B describing the pressure-head dependence of the transformation rate was set to 0.25, based on Boesten.²⁹ Notice that parameter B was originally obtained for the relationship $f_\theta = (\theta/\theta_{ref})^B$. We converted the value given by Boesten²⁹ to the value required in eqn (13) using the measured water retention characteristic.

The transpiration stream concentration factor for pesticide uptake, f_{uc} , was initially set to 0.5, which is the average of values reported in Briggs *et al.*³⁰ As the range of probable values for f_{uc} is considerable, it is considered a calibration parameter. For ethoprophos the range is 0–1, as it is a non-ionic substance. Bentazone, on the other hand, is an ionic substance, so the range to be considered is as large as 0–3.³¹

The diffusion coefficients of ethoprophos and bentazone in water were set to 3.5×10^{-5} m² day⁻¹.³¹ The effective diffusion coefficient of pesticide in free air was estimated at 0.4 m² day⁻¹.⁸ The Henry coefficient was calculated from the water solubility and saturated vapour pressure published by Tomlin.³² Its value was 6.1×10^{-6} m³ m⁻³ for ethoprophos and 7.9×10^{-8} m³ m⁻³ for bentazone. Following Jury *et al.*²⁰ and Freijer *et al.*,⁸ surface volatilization is simulated using a stagnant air boundary layer thickness, d ,

TABLE 4
Half-life under Reference Conditions and Temperature Dependence of Transformation using Different Fitting Procedures

Parameter	Ethoprophos		Bentazone	
	ln-transformed	Non-linear	ln-transformed	Non-linear
E_a (kJ mol ⁻¹) ^a	67	67	90	121
γ (—)	0.094	0.094	0.126	0.170
DT_{50} , A layer (day) ^b	105	83	28	16
DT_{50} , B layer (day) ^b	186	210	2610	1880
DT_{50} , C layer (day) ^b	146	125	27	14

^a Molar energy of activation in the Arrhenius equation.

^b At $T = 20^\circ\text{C}$.

of 0.005 m. The surface resistance for volatilization was initially set to 10 m^{-1} . Its final value was obtained by calibration.

2.4 Model calibration

Calibration is necessary for parameters that cannot be measured independently. Model Calibration may also be necessary when only generic (i.e. not site-specific) model parameters are available. In the present study, only a limited number of parameters were obtained by calibration. Moreover, a logical sequence for calibration was adopted based on the strength of interactions between hydrology, soil chemical transport and pesticide behaviour. Table 5 shows the parameters that were calibrated.

When comparing the model predictions with the observed data, both qualitative and quantitative techniques were employed. Quantitative techniques try to express the agreement between model and data numerically, while qualitative techniques are based on (subjective) visual inspection of the results. As indicated by Janssen and Heuberger³³ results from both techniques should be interpreted with due care, and only a combination of both techniques is bound to be successful. In this study we used two performance measures, i.e. the Normalized Root Means Square Error (NRMSE) and the Modelling Efficiency (ME):

$$\text{NRMSE} = \frac{\sqrt{\sum_{i=1}^n (P_i - O_i)^2 / n}}{\bar{O}} \quad (18)$$

$$\text{ME} = \frac{\sum_{i=1}^n (O_i - \bar{O})^2 - \sum_{i=1}^n (P_i - \bar{P})^2}{\sum_{i=1}^n (O_i - \bar{O})^2} \quad (19)$$

where P_i and O_i denote the predicted and observed values i , \bar{O} and \bar{P} are their means, and n is the number of observations. The Normalized Root Mean Square Error expresses the spread around the measurements, while the Modelling Efficiency indicates whether the

model describes the data better than simply the average of the predictions. Optimal values are zero and one, respectively.

3 RESULTS AND DISCUSSION

3.1 Hydrology

Measurements of groundwater levels and soil water contents were available for comparison with the simulations. These data and the simulation results are presented in Fig. 1 and Fig. 2. Statistical performance measures are presented in Table 6.

Model parameters for the first run are given in Section 2.3. Both Fig. 1 and Table 6 show that there is considerable disagreement between the simulated and measured groundwater levels. This is not surprising, because we started with generic relationships between groundwater level and drainage.²⁷ As there was no information on the local hydrological situation, parameters for this relationship could only be obtained by calibration. We decided to use an automated calibration procedure as described in Section 2.3. Final optimized parameters were: $a_b = -0.042 \text{ m day}^{-1}$, $b_b = -3.8 \text{ m}^{-1}$ and $c_b = -0.001 \text{ m day}^{-1}$. The simulation of groundwater levels is now quite reasonable, both statistically and derived from qualitative judgement. Notice that the peak around day 100 is not reproduced by the model, and that there is almost no rainfall preceding this groundwater rise. Probably, an external factor has caused this particular rise.

Figure 2 shows that soil water contents were overestimated in the 0.3–0.6 m layer. This implies that the measured water retention characteristics are not representative for the field profile. The reason for this may be that the samples for the determination of the water retention characteristics were too small to be representative for the field soil. The measured saturated soil water content for the second layer was almost as high as that of the upper soil layer (Table 2). At the same time, both the profile description and measurements of the organic matter content indicate that it is improbable for the hydraulic properties of the middle soil layer to resemble those of the topsoil. Therefore, we

TABLE 5
PESTRAS Parameters that were Calibrated

#	Parameter	Description	Calibration criterion	Eqn
1	a_b, b_b and c_b	Groundwater level-drainage parameters	Groundwater-level	(3)
2	θ_s	Saturated water content	Water content	— ^a
3	L	Dispersion length	Bromide content	(6)
4	f_{uc}, Br^-	Uptake factor for bromide	Bromide content	(14)
5	R_v	Transport resistance	Total mass of pesticide	(16)
6	$f_{uc, pest}$	Uptake factor ethoprophos and bentazone	Pesticide content	(14)

^a Equations specified by Van Genuchten.²¹

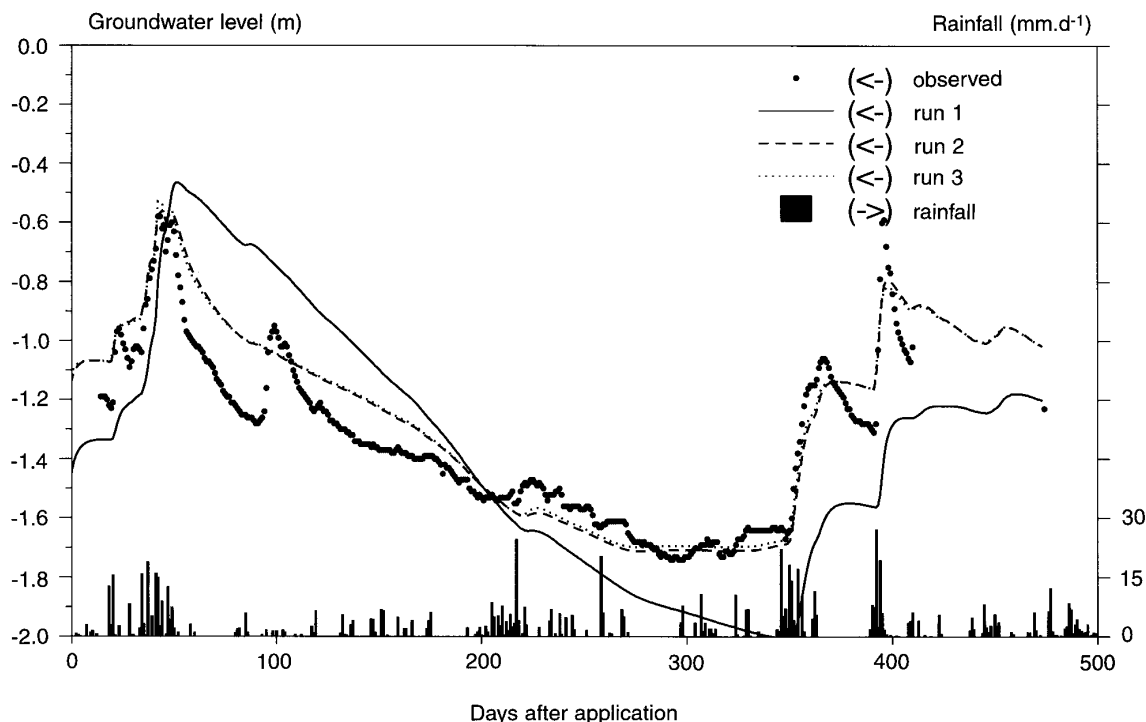


Fig. 1. Measured and simulated groundwater levels. Run 1: Before calibration; run 2: groundwater level–drainage relationship adjusted; run 3: profile description adjusted.

decided to perform a third run using a two-layer hydraulic system, i.e. the 0.3–0.6 m layer was given the same hydraulic properties as the lower soil layer. Figure 2 shows that there is considerable improvement of the simulated soil water contents. Notice that the groundwater levels were almost unaffected by dropping the second layer.

Although there remain some differences between the model predictions and the observations, further calibration was not carried out. The reason for this is that soil water contents were measured at a limited number of times, so that it was difficult to judge model response in terms of temporal variability. Moreover, the aim of the application of the hydrological part of the model was not to provide a pure fit to the measured data but

to quantify the most important water balance components. Table 7 shows that the water balance was hardly affected by the calibration procedure. Also the occurrence of unfavourable conditions for pesticide transformation was not or hardly affected, as indicated by the time-integrated average value of parameter f_p in eqn (13).

3.2 Bromide

There were two calibration parameters relevant to bromide transport, i.e. the dispersion length, L , and the transpiration concentration stream factor, $f_{uc, Br}$. As a first step we optimized the dispersion length. The range

TABLE 6
Normalized Root Mean Square Error (NRMSE) and Modelling Efficiency (ME) of Simulated Groundwater Levels and Soil Water Contents for Three Model Runs^a

	Groundwater level			Soil water content		
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
NRMSE	0.2401	0.0858	0.0889	0.3594	0.2808	0.1843
ME	−0.3069	0.8331	0.8210	−0.0544	0.3563	0.7229

^a Run 1: Before calibration; Run 2: Relationship between groundwater level and drainage adjusted; Run 3: profile description adjusted.

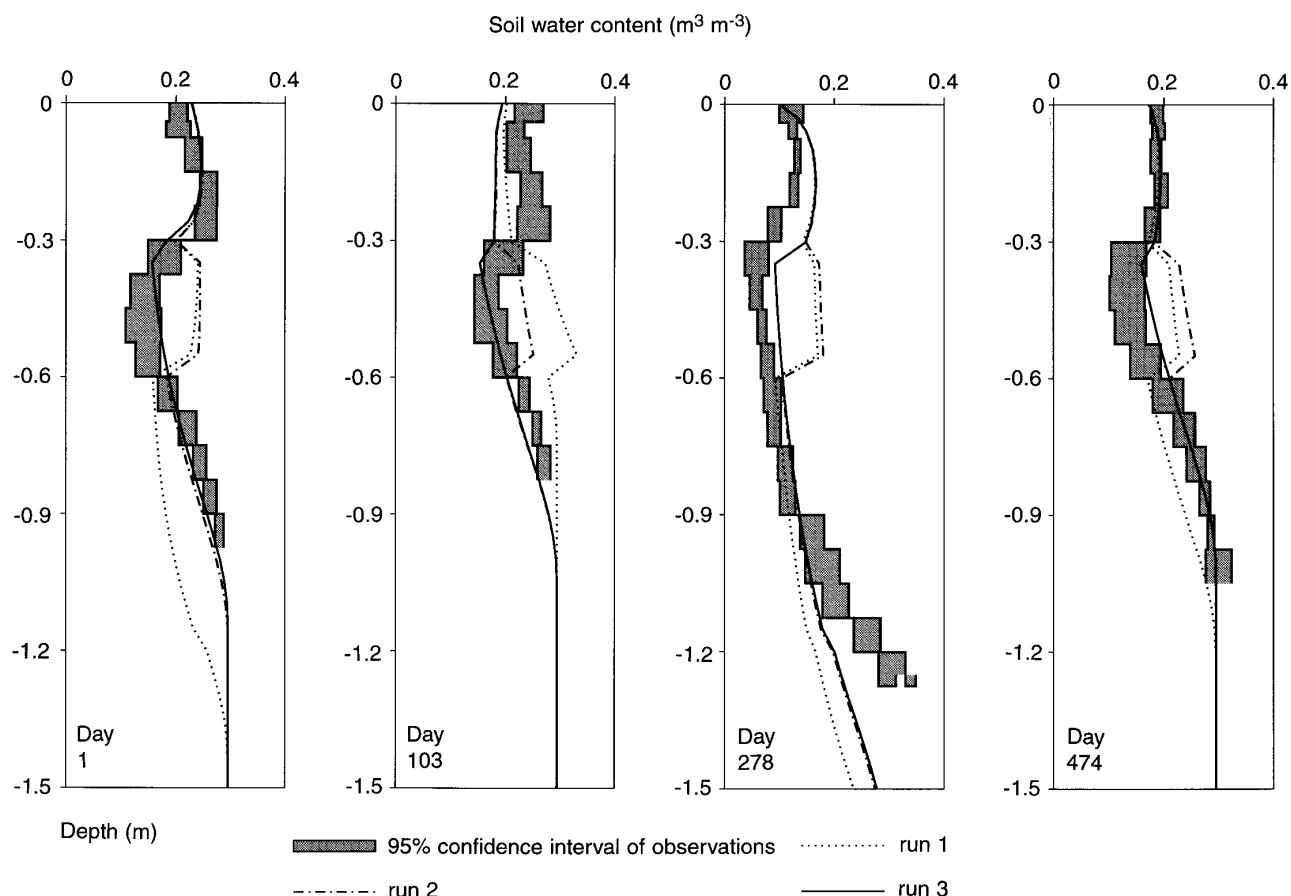


Fig. 2. Simulated and measured soil water profiles at 1, 103, 278 and 474 days after application. See Fig. 1 for explanation of model runs.

considered was 0.025–0.10 m, which is the range given by Van Ommen *et al.*²⁴ Figure 3 gives the simulated and observed bromide profiles at 103 and 278 days after application. The lower and upper bounds of the observed values are the approximate 95% confidence intervals, calculated by subtracting and adding 2.13 times the standard error of the average observed concentration. As the overall performance could not objectively be judged from graphical comparison, we decided

to rely fully on the statistical performance measures listed in Table 8. From these measures it followed that a dispersion length of 0.075 m could best be used in the rest of the simulations. This value is somewhat higher than the value used by Tiktak *et al.*^{9,10} in regional-scale simulations of pesticide leaching.

In a second step the transpiration concentration stream factor was calibrated. These results are also given in Fig. 3 and Table 8. Table 8 shows that the

TABLE 7
Overview of Results from the Hydrological Submodel

Run ^a	Components of the Calculated Water Balance ^b (mm)								f_p ^c (–)	
	<i>P</i>	<i>ET</i> *	<i>E_T</i>	<i>E_s</i>	<i>q</i> ₂₅	<i>E</i> ₅₀	<i>q</i> ₁₀₀	ΔW	<i>Avg</i>	<i>Max</i>
1	768	616	334	99	451	359	339	–4	0.961	0.719
2	768	616	334	98	452	356	338	–2	0.961	0.700
3	768	616	334	98	447	351	337	–1	0.963	0.719

^a See Table 6 for explanation of model runs.

^b Calculated for the period 22 November 1990 until 9 March 1992. *P*: precipitation; *ET**: reference evapotranspiration; *E_T*: actual transpiration; *E_s*: actual soil evaporation; *q*₂₅: drainage at 0.25 m depth; *q*₅₀: drainage at 0.5 m depth; *q*₁₀₀: drainage at 1 m depth; ΔW : storage change.

^c f_p : pressure head dependence of pesticide transformation [eqn (13)].

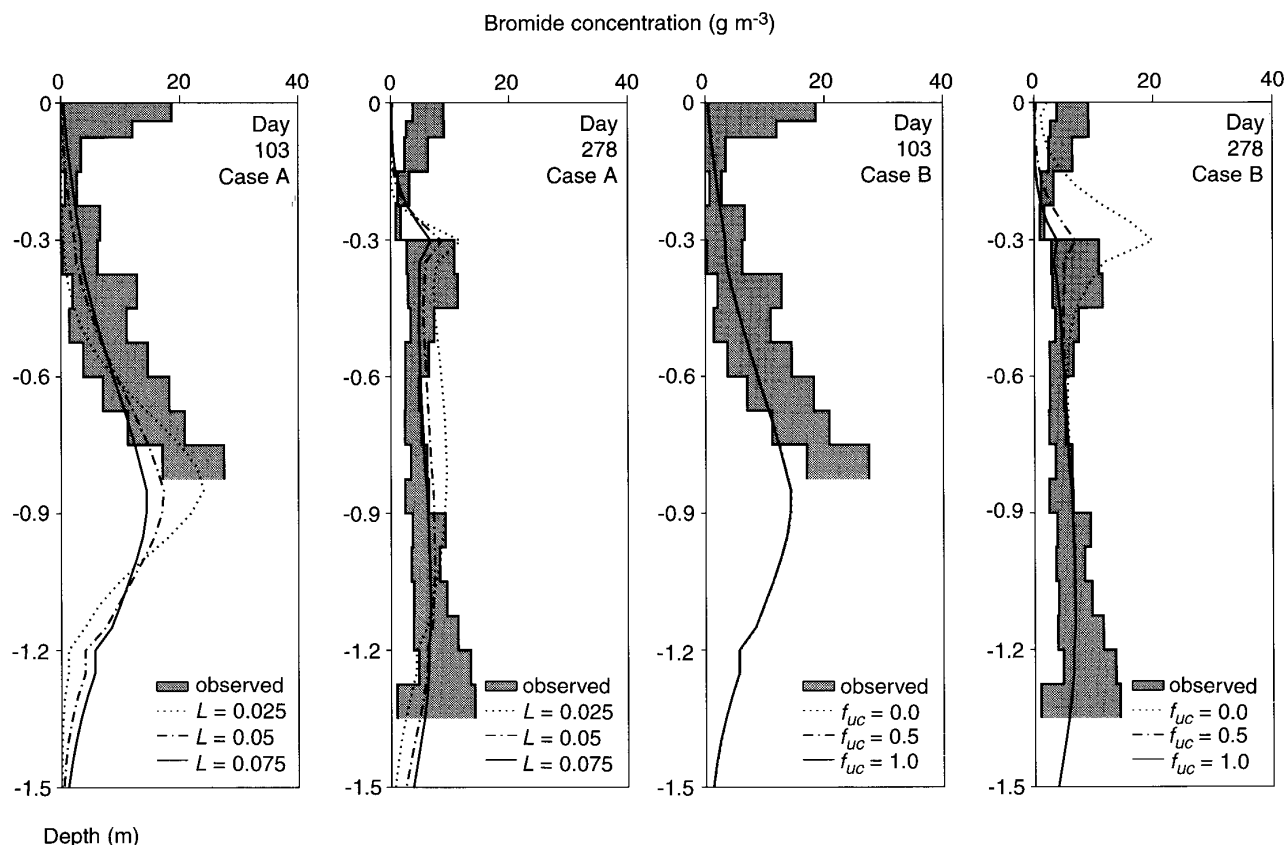


Fig. 3. Simulated and observed concentration of bromide as a function of depth at 103 and 278 days after application. Case A: effect of dispersion length; case B: effect of transpiration concentration stream factor.

statistical performance measures were not affected by $f_{uc, Br-}$. Figure 3, however, shows considerable differences between model results for day 278. From this graph it follows that bromide concentrations were seriously overestimated in the 0.15–0.45 m soil layer when $f_{uc, Br-}$ was set to zero. The predictions for day 103 were not sensitive to $f_{uc, Br-}$ as this is a winter situation with almost no water uptake. Notice that the observations

show elevated concentrations of bromide in the upper soil layer that are not predicted by the model. This is most probably due to physical non-equilibrium conditions resulting from diffusion-limited mass transfer.³⁴

Table 8 shows the mass balance for the five model runs. The effect of the dispersion length on the mass balance is considerable. Apparently, a slightly different distribution of bromide yields a significant difference in

TABLE 8
Statistical Performance Measures and Mass Balance for the Bromide Simulations

$L(m)$	$f_{uc}(-)$	$NRMSE^a$	ME_a	<i>Mass balance (% of applied bromide)^b</i>		
				fr_{upt}	fr_l	fr_{sys}
<i>Case A: Effect of dispersion length, L</i>						
0.025	0.5	2.9	0.28	16.5	82.7	0.8
0.050	0.5	2.4	0.53	22.4	74.5	3.1
0.075	0.5	2.0	0.68	24.9	70.5	4.6
<i>Case B: Effect of transpiration concentration stream factor, f_{uc}</i>						
0.075	0.0	2.0	0.68	0.0	89.4	10.6
0.075	0.5	2.0	0.68	24.9	70.5	4.6
0.075	1.0	2.0	0.68	30.2	66.2	3.6

^a Calculated for 1, 103, 278 and 474 days after application.

^b fr_{upt} is fraction taken up; fr_l is fraction leached; fr_{sys} is fraction left in the upper metre.

bromide uptake. Notice that a considerable fraction of the total dosage of bromide was taken up. This complicates the interpretation of bromide profiles in a cropped field situation. Nevertheless, the general agreement between the model and the observations indicates that preferential flow is only of limited importance for this field soil. This confirms the observations by Hamminga *et al.*³⁵ who did not find indications for fingered flow, despite the fact that the soil was known to be water-repellent.

3.3 Ethoprophos

As discussed before, different values for DT_{50} and K_{om} may be derived from the experimental data. Although arbitrarily, we decided to use pesticide properties obtained by non-linear curve fitting, so DT_{50} was set to 83 days and K_{om} to 63 litre kg^{-1} . The only calibration parameter was the transport resistance for surface volatilization, R_v . This parameter was fitted using the observed areic mass of pesticide in the soil system. Its optimized value was 1.4×10^{-4} day m^{-1} . Results are shown in Table 9 and Fig. 4.

Figure 4 shows a rapid decrease of ethoprophos due to surface volatilization directly after application. This

fast decrease stops after the first rainfall; almost 60% of the applied dose has then disappeared (Table 9). This implies that a significant fraction of surface-applied pesticides may disappear by volatilization, even if they are only moderately volatile ($10^{-6} < K_H < 10^{-5}$). Ignorance of this process will thus overestimate the leaching of pesticides. However, although the model is able to reproduce the observed fast decrease of ethoprophos, predictions of surface volatilization remain too uncertain to be applied for regional-scale modelling. The major restriction is that not enough experimental data are available for a reliable parameterization of this sub-model. Moreover, the transport resistance is highly dependent upon the atmospheric conditions after application.²⁰

Both the measurements and the model indicate that there was no ethoprophos below 0.3 m depth at the end of the experiment, so the leaching potential of ethoprophos is negligible. Nevertheless, the movement of ethoprophos is slightly overestimated (Fig. 4). This may be caused by the adsorption in the field being stronger than expected on the basis of 24-h equilibrium isotherms obtained in the laboratory. A possible explanation is that sorption in soils is a non-instantaneous process^{36,37} resulting in an increase of the distribution coefficient with time.³⁸ The latter authors showed that

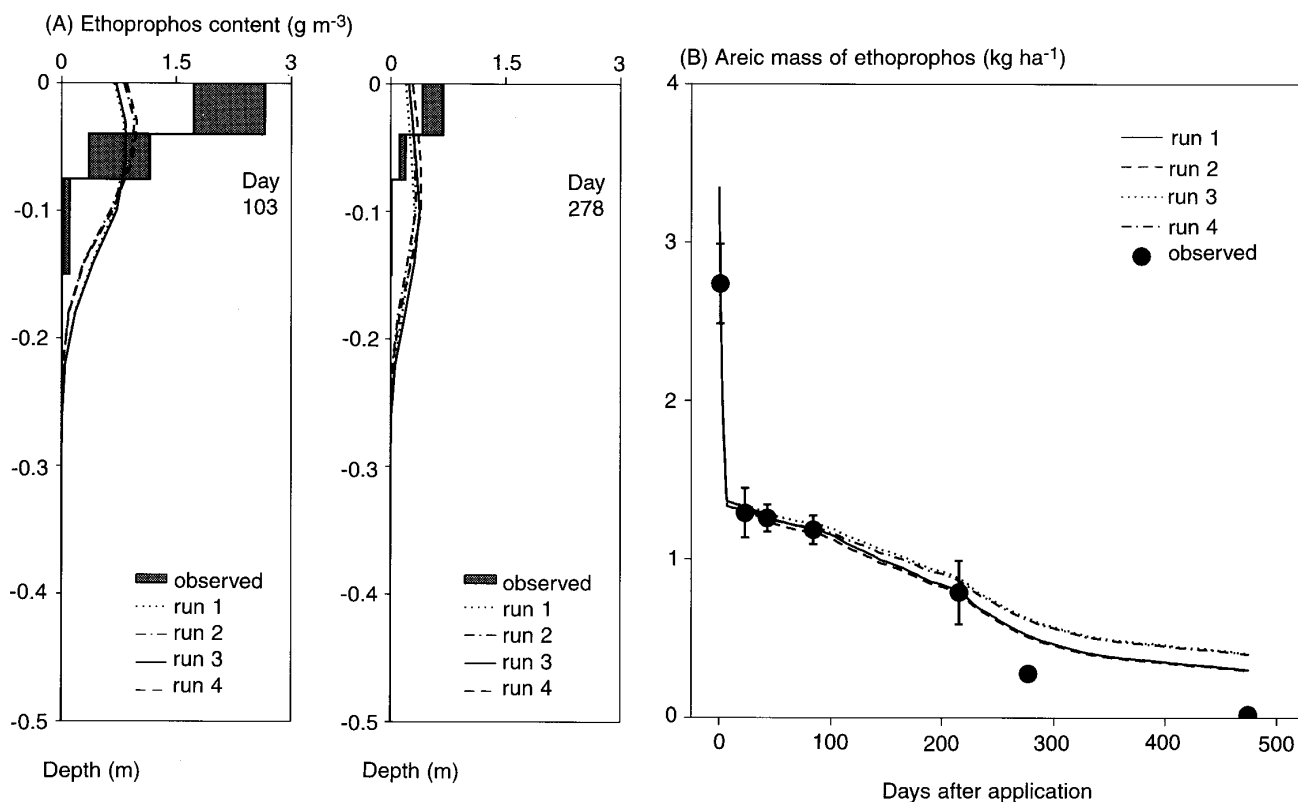


Fig. 4. (A): Simulated and observed concentration of etoprophos as a function of depth at 103 and 278 days after application. (B): Areic mass of etoprophos as a function of time. See text for explanation of runs. Run 1: DT_{50} = 83 days and K_{om} = 63 litre kg^{-1} ; run 2: DT_{50} = 83 days and K_{om} = 90 litre kg^{-1} ; run 3: DT_{50} = 105 days and K_{om} = 63 litre kg^{-1} ; run 4: DT_{50} = 105 days and K_{om} = 90 litre kg^{-1} .

TABLE 9
Statistical Performance Measures and Mass Balance for Ethoprophos Simulations

K_{om} (litre kg^{-1})	DT_{50} (days)	NRMSE ^a	ME ^a	Mass balance (% of applied ethoprophos) ^b				
				fr_{vol}	fr_{tran}	fr_{upt}	fr_{sys}	fr_l
63	83	0.768	0.169	59.2	29.9	1.9	9.0	$<10^{-6}$

^a Calculated for 1, 103, 278 and 474 days after application.

^b fr_{vol} is fraction volatilized; fr_{tran} is fraction transformed; fr_{upt} is fraction taken up; fr_{sys} is fraction left in system; fr_l is fraction leached from the upper metre of the soil profile.

the distribution coefficient was approximately 2 to 40 times greater than the 24-h K_F , depending on the time after application.

The areic mass of ethoprophos was reproduced by the model until 214 days after application (Fig. 4). From this day onwards, the model overestimated the residual mass. As transformation is the most important loss pathway for ethoprophos during the later stages of the experiment (Table 9), it can be concluded that this is caused by underestimation of the rate of transformation. There are a number of explanations for this phenomenon. First, the pressure-head dependency of transformation may have been overestimated. The occurrence of low soil-water pressure heads coincides with the time that model predictions started to deviate from the measured areic mass. A run with f_p set to zero, however, showed almost no difference with the presented results. An alternative explanation is accelerated transformation due to adaptation of the microbial population. Smelt *et al.*³⁹ found higher rates of transformation of ethoprophos from annually treated soils compared with soils not previously treated. As PESTRAS does not account for this effect, this hypothesis could not be tested.

Four simulations were done to show the effect of different fitting procedures for calculating DT_{50} and K_{om} (Section 2.3). Figure 4 shows limited differences between the four model runs. This is due to the fact that both

K_{om} and DT_{50} were in a range where, according to an earlier sensitivity analyses,⁴⁰ model output was relatively insensitive to variations of these parameters.

3.4 Bentazone

As with the ethoprophos simulations, pesticide properties obtained by non-linear curve fitting were used, so K_{om} was set to 2.8 litre kg^{-1} and DT_{50} was set to 16 days. With the R_v values obtained in the ethoprophos simulations, the surface volatilization fluxes of bentazone were negligible. Therefore, to speed up the calculations the gas transport sub-model was switched off.

Simulated and measured concentration profiles are shown in Fig. 5. Generally, the model results are within the approximate 95% confidence intervals of the observations. Both the model and the observations indicate significant transport of bentazone to the subsoil compared to ethoprophos. Approximately 30% of the applied dose leached below the depth of 1 m (Table 10). At 214 days after application, the model overestimated the bentazone concentration in the topsoil. At the end of the experiment (day 474), all bentazone was removed from the system according to the observations, while the model still predicted some bentazone to be present in the soil system.

The most important loss pathway for bentazone is transformation (Table 10). The depth dependence of

TABLE 10
Statistical Performance Measures and Mass Balance for the Three Model Runs Described in Section 3.4

$f_z(-)^a$	$f_{uc}(-)$	NRMSE ^b	ME ^b	Mass balance (% of applied bentazone) ^c				
				fr_{vol}	fr_{tran}	fr_{upt}	fr_{sys}	fr_l^d
0.00	0.5	2.055	0.414	0.0	66.7	23.3	10.1	30.4
0.25	0.5	2.139	0.430	0.0	73.4	21.0	5.6	23.5
0.00	2.0	1.987	0.511	0.0	59.8	30.9	9.3	29.6

^a f_z for the 0.5–1.0-m soil layer. Other values not adjusted.

^b Calculated for 1, 103, 278 and 474 days after application.

^c fr_{vol} is fraction volatilized; fr_{tran} is fraction transformed; fr_{upt} is fraction taken up; fr_{sys} is fraction left in system; fr_l is fraction leached from the upper metre of the soil profile.

^d As the total mass balance applies to the 0–2-m soil layer, this flux may not be considered part of the total mass balance. Consequently, the terms do not add up to 100%.

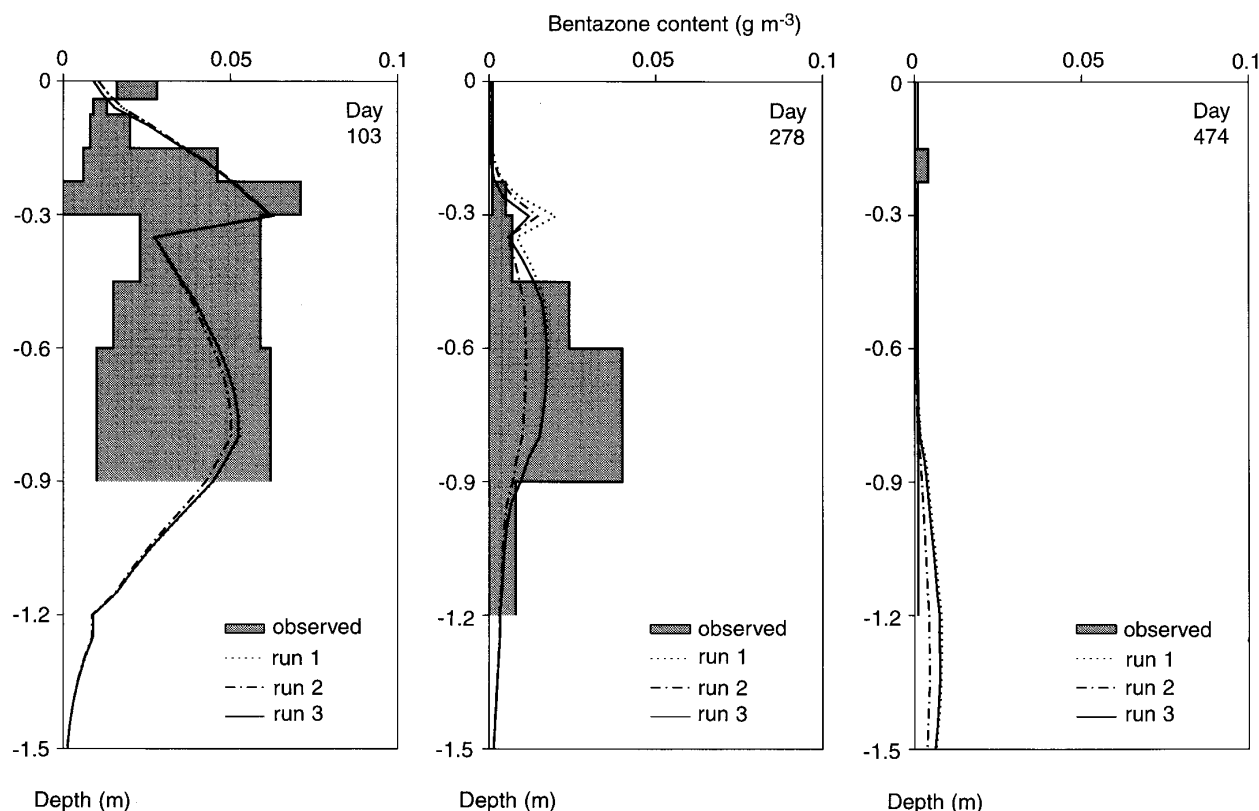


Fig. 5. Simulated and observed concentration of bentazone as a function of depth at 103, 278 and 474 days after application. Run 1: $f_z = 0.00$ and $f_{uc} = 0.5$; run 2: $f_z = 0.25$ and $f_{uc} = 0.5$; run 3: $f_z = 0.00$ and $f_{uc} = 2.0$.

transformation as derived from the laboratory incubation experiments (Table 4) is in contradiction with the standard application of PESTRAS^{9,10} where no transformation below 1 m was assumed, based on literature data.¹⁹ As a result, the model calculated a significant fraction of bentazone (21% of the applied dose) to be removed by transformation from the 1–2-m soil layer. The laboratory experiments indicated no transformation in the 0.5–1-m soil layer. The already mentioned overestimation of the calculated bentazone concentration at 474 days after application probably results from transformation rates being underestimated for this particular soil layer. To check this, an additional simulation was performed with f_z set to 0.25 between 0.5 and 1 m depth. Results indicate better agreement at the end of the experiment (Fig. 5), but at day 278 the calculated concentration profile diverged from the average measured concentration. It can be concluded that the simulations do not contradict the results from the incubation experiments. An explanation for the curious depth dependence of transformation cannot be found in the literature. A possible explanation could be that in this soil there are two distinct microbiological populations: In the topsoil, bentazone is transformed aerobically, while in the 1–2-m soil layer bentazone is primarily transformed by anaerobic or micro-aerophilic

organisms. In the middle soil layer, where aerobic and anaerobic conditions alternate, none of the two populations may have been adjusted.

The overestimation of bentazone contents in the root zone at day 278 is likely to be caused by underestimation of the transpiration concentration stream factor, f_{uc} . As bentazone is an ionic substance, f_{uc} is highly uncertain. Shone and Wood,⁴¹ for example, empirically derived a f_{uc} value of 3.1 for the 2,4-D anion, so preferential uptake of bentazone cannot be excluded. An additional simulation with f_{uc} set to 2 was carried out to test this hypothesis. Figure 5 and Table 10 indeed show that the model performed better with a higher f_{uc} value. Notice that, although the fraction of bentazone taken up increased, the fraction leached below 1 m was hardly affected, due to competition between transformation and uptake. This phenomenon was already reported by Tiktak *et al.*^{9,10}

With the transpiration concentration stream factor set to 2, the effect of fitting procedures in the interpretation of laboratory experiments was analysed. As the differences were minor, results are not presented here. The marginal differences were caused by the fact that the higher value of γ was compensated for by a lower value of DT_{50} . This resulted in almost equal transformation rates in the temperature range 5–15°C.

3.5 Effect of calibration procedure on major indices of pesticide behaviour

Although, in this study, PESTRAS was used as a field-scale pesticide transport assessment tool, it was primarily developed for simulating pesticide leaching on a regional scale.^{9,10} It is therefore interesting to quantify the effect of the calibration procedure on indices of pesticide leaching and accumulation, i.e. the maximum concentration of pesticide in the 1–2-m soil layer (c_{max}) and the residual fraction in the plough layer at one year after application (fr_{pl}). To accomplish this, a number of simulations were carried out with generic parameter values instead of the calibrated or on-site measured parameter values. Results are shown in Table 11.

The use of generic pesticide degradation parameters had a major impact on both the residual fraction of ethoprophos and the maximum concentration of bentazone. With default values for the half-life, the accumulation of ethoprophos was underestimated by a factor of 7. With default values for the temperature dependence of transformation, the leaching of bentazone was also underestimated, but it was overestimated when default values for the depth dependence of transformation were used. Generic pesticide properties are usually averages of values obtained from a series of laboratory studies with a considerable standard deviation. The default half-life of ethoprophos, for example, was 32 days with a standard deviation of 24 days.⁴² This example shows that predictions of pesticide accumulation and leaching on a regional scale should be accompanied by estimates of confidence intervals due to uncertain pesticide properties.^{43,44} The effect of ignoring surface volatilization of ethoprophos was tremendous. This implies that leaching of surface-applied moderately volatile pesticides may be overestimated. As mentioned before, this aspect needs further attention.

Some other parameters (dispersion length, transpiration concentration stream factor) affected the two indices, but to a far lesser extent. Conclusions on the effect of these parameters, however, must be made with care. The transpiration concentration stream factor, for example, may be much more important for pesticides that are applied in spring. Also the effect of the relationship between the groundwater level and drainage on bentazone leaching is ambiguous: The effect is such that the peak concentration is not affected, but with generic groundwater level–drainage relationships, the peak concentration is retarded due to slower downward transport.

4 CONCLUSIONS

For the soil and conditions in this field study, the PESTRAS model was found to predict the movement of a non-adsorbed compound (bromide) and two pesticides (ethoprophos and bentazone) reasonably well when site-specific parameter values were used. When generic parameter values were used, the model predictions sometimes deviated strongly from the observed data. This implies that predictions of pesticide leaching on a regional scale, as carried out by e.g. Tiktak *et al.*,^{9,10} should be accompanied by estimations of confidence intervals obtained by appropriate uncertainty analyses.⁴⁴

The observed bromide profiles could only be reproduced if it was assumed that a considerable fraction of the applied bromide was taken up. This complicated the interpretation of the observed bromide profiles in this cropped field soil. Nevertheless, the bromide simulations showed that the convection–dispersion model was able to describe the observed concentration profiles,

TABLE 11
Effect of using Generic Data instead of On-Site Measured or Calibrated Data on the Maximum Concentration of Pesticide in the Upper Groundwater (c_{max}) and the Fraction of Pesticide in the Plough Layer (fr_{pl})

#	Parameter considered	Ethoprophos		Bentazone	
		c_{max} ($\mu\text{g litre}^{-1}$)	fr_{pl} (%)	c_{max} ($\mu\text{g litre}^{-1}$)	fr_{pl} (%)
1	Site-specific data	0	9.7	15.2	0.04
3	pF, $K(h)$ by transfer function	0	9.1	12.9	0.07
2	a_b , b_b , c_b from De Visser and De Vries (1989)	0	9.0	15.4	0.04
3	L set to 0.05 m (default value)	0	10.19	18.2	0.01
4	K_{om} from default database	0	9.2	18.8	0.02
5	DT_{50} from default database	0	1.41	15.2	0.04
6	K_H set to zero	0	22.28	15.2	0.04
7	γ set to 0.08 (default value)	0	8.5	2.6	0.01
7	f_{uc} set to 0.5 (default value)	0	9.7	17.8	0.16
8	f_z set to default values	0	9.7	35.7	0.01

indicating that preferential flow was not an important process in this sandy soil.

Almost 60% of the applied dose of ethoprophos volatilized directly after application. Although PESTRAS was able to reproduce this observed fast decrease of ethoprophos, predictions of volatilization of surface-applied pesticides remain too uncertain to be applied for regional-scale modelling. Not enough data are available for a reliable parameterization of this sub-model, so there is an urgent need for research in this field. Both the simulations and the observations indicated that there was no ethoprophos below 0.3 m depth, so the leaching potential was negligible. The movement of ethoprophos was slightly overestimated, probably due to ignoring long-term sorption kinetics. Transformation rates were reasonably described until 214 days after application. From that day onwards, transformation in the field was faster than predicted, probably due to adaptation of the microbial population.

The concentration profiles of bentazone could only be explained if it was assumed that bentazone was taken up preferentially ($f_{uc} > 1$). The effect of uptake on leaching, however, was negligible due to competition between transformation and uptake. With the atypical depth dependence of transformation measured on-site, we could reproduce the observed bentazone profiles. The model calculated almost 30% of the applied bentazone to leach below 1 m depth. However, almost 20% of the total dose disappeared from the 1–2-m soil layer by transformation under micro-aerobic to anaerobic conditions. As anaerobic transformation is a key process in predicting the risk of contamination of drinking-water wells by pesticides, research on transformation in the saturated zone is required. The occurrence of bentazone in some drinking-water wells⁴⁵ at least indicates that anaerobic transformation does not always occur.

In this study, the procedure of deriving pesticide properties from the original sorption and dissipation data did not affect the simulations to a great extent. This conclusion, however, may not be generally applicable, as indicated by, for example, Boekhold *et al.*⁴⁶ With results from non-linear curve fitting or linear regression of ln-transformed data they could either reject or validate the model. Work should be done to reduce subjectivity in deriving model inputs.

The conclusions in this paper pertain to the current application only. As PESTRAS is developed for simulating pesticide leaching on a regional scale, the model must be evaluated in a broader range of soils, pesticides and hydrological conditions.

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